

NON-CHROMATE METAL SURFACE ETCHING SOLUTIONS

TO WHOM IT MAY CONCERN:

BE IT KNOWN THAT (1) WAYNE C. TUCKER, (2) MARIA G. MEDEIROS, employees of the United States Government, citizens of the United States of America, and resident of (1) Exeter, County of Washington, State of Rhode Island, (2) Bristol, County of Bristol, Rhode Island; and, (3) RICHARD BROWN, citizen of the United Kingdom and resident of Wakefield, Washington County, Rhode Island have invented certain new and useful improvements entitled as set forth above of which the following is a specification:

PRITHVI C. LALL, ESQ.
Reg. No. 26192
Naval Undersea Warfare Center
Division, Newport
Newport, Rhode Island 02841-1708
TEL: 401-832-4736
FAX: 401-832-1231

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3 NON-CHROMATE METAL SURFACE ETCHING SOLUTIONS

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5 STATEMENT OF GOVERNMENT INTEREST

6 The invention described herein may be manufactured and
7 used by or for the Government of the United States of America for
8 Governmental purposes without the payment of any royalty thereon
9 or therefor.

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11 CROSS REFERENCE TO OTHER PATENTS APPLICATIONS.

12 This patent application is co-pending with one related
13 patent applications entitled NON-CHROMATE COVERSION COATING
14 (Attorney Docket No. 82602), by the same inventors as this
15 application.

16

17 BACKGROUND OF THE INVENTION

18 (1) FIELD OF THE INVENTION

19 The present invention relates to a non-chromate metal
20 surface treating composition for increasing the adhesion of a
21 metal's surface to any one of a group of layers applied thereto,
22 such as corrosion resistant layers, and method of applying same.
23 More particularly, the present invention relates to a metal
24 surface etching solution wherein a chromate, such as sodium
25 dichromate dehydrate, or an oxide of chromium, such as chromium

1 trioxide, is replaced with a titanate, namely sodium metatitanate
2 or an oxide of titanium, namely, titanium dioxide, respectively.

3 (2) DESCRIPTION OF THE PRIOR ART

4 It is known that solutions containing hexavalent chromium
5 can be used to treat the surface of a metal as etching agents to
6 increase the adhesion of layers which are subsequently applied
7 thereto, such as protective coatings. However, although
8 hexavalent chromium-containing solutions are efficient etching
9 agents, they are also highly toxic and adversely affect the
10 environment and human health. For this reason, many chromate-
11 free solutions for treating metal surfaces have been proposed.

12 Thus, various non-chromate metal surface treatments, such as
13 disclosed in Tomlinson U.S. Patent No. 5,759,244, the disclosure
14 of which is incorporated by reference herein, have been disclosed
15 which can increase the adhesion of a metal's surface to a layer
16 subsequently applied thereto. Many of these metal treatments are
17 based on group IV-B metals such as titanium, zirconium and
18 hafnium. For example, U.S. Patent No. 5,868,872 to Karmaschek et
19 al discloses a chromium-free aqueous bath solution for non-rinse
20 treatment of aluminum and its alloys. The solution comprises
21 zirconium and titanium, orthophosphate, fluoride and a water-
22 soluble or homogeneously water-dispersible organic film former.
23 When applied, the solution is dried on the surface of the
24 aluminum without rinsing. Similarly, U.S. Patent No. 5,897,716
25 to Reghi et al discloses a chemically and thermally stable

1 chromate-free aqueous liquid treatment for metals which increases
2 the adhesion of protective layers to the metals' surfaces. The
3 chromate-free aqueous liquid comprises components selected from
4 the group consisting of H_2TiF_6 , H_2ZrF_6 , H_2HfF_6 , H_2SiF_6 , H_2GeF_6 ,
5 H_2SnF_6 , HBF_4 , and mixtures thereof.

6 The shortcoming of conventional non-chromate metal surface
7 treatments, such as those described above, is that they cannot be
8 integrated into and employed in place of chromium-containing
9 compounds in current metal treatment solutions which otherwise
10 would contain chromium. As such, conventional non-chromate metal
11 surface treatments are usually so different from previously
12 employed chromate-containing metal surface treatments that
13 significant changes are required to be made in the metal treating
14 process and in the production of the metal surface treatment
15 itself. These changes can amount substantial expenditures and
16 usually require additional approval from Department of the Navy.
17 Thus, there is a need for "drop-in replacements" that can be
18 employed in place of chromium-containing compounds, such as
19 sodium dichromate, now used in conventional chromate-containing
20 metal treatment solutions. "Drop-in replacement" refers to a
21 compound that can be employed in a metal surface treatment
22 solution in lieu of a chromium-containing compound without
23 requiring any or substantial changes in the make-up of the metal
24 surface treatment process or metal surface treatment solution.

SUMMARY OF THE INVENTION

1 It is a primary object of the invention to provide a non-
2 chromate metal surface treatment solution for increasing the
3 adhesion of a layer, such as a corrosion resistant layer, to a
4 metal's surface wherein the solution contains a titanate or
5 titanium dioxide in place of a chromium-containing compound.

6 It is a further primary object of the invention to provide a
7 "drop-in replacement" for a chromium-containing compound that can
8 be employed in a metal surface treatment solution which otherwise
9 would include chromium.

10 Another object of the invention is to provide a method of
11 increasing the adhesion of a metal's surface to a layer, such as
12 a protective or corrosion resistant layer, applied thereto.

13 The objects of the invention are accomplished by providing a
14 highly effective, non-chromate metal surface treatment solution
15 which includes a titanate, such as sodium metatitanate or
16 potassium titanate, or titanium dioxide in lieu of a chromium-
17 containing compound in a metal surface treatment solution that
18 otherwise would include chromium. More particularly, the
19 invention relates to a non-chromate metal surface etching
20 solution for etching metals, specifically, aluminum, aluminum
21 alloys, stainless steel, titanium and titanium alloys, to
22 increase the adhesion properties of a particular metal's surface.

23 The present invention is developed on the basis of findings
24 that the adhesion of a layer or coating, such as corrosion

1 resistant coating, to a metal's surface can be increased by
2 bathing a metal substrate in an aqueous solution which contains a
3 chromium-containing compound. Specifically, for example, it is
4 known that a solution containing distilled or deionized water,
5 sulfuric acid, seed aluminum and sodium dichromate dihydrate
6 creates a superb etching solution for aluminum and aluminum
7 alloys. It is further known that a solution containing chromium
8 trioxide and deionized water creates a superb etching solution
9 for stainless steel and titanium. It is believed that the
10 chromium-containing compound in each of the foregoing etching
11 solutions provides increased adhesion to the respective metal
12 surface by providing a contact surface chemistry and allowing for
13 ionic bonding.

14 Test results show that a metal tested without being treated
15 with an etching solution has poor durability and weak boundry
16 layer. For example, untreated aluminum has weak boundry layer
17 and weak oxides; untreated stainless steel has controlled surface
18 properties; and untreated titanium has controlled surface
19 properties. However, since personal exposure limits (PEL) for
20 chromates is 0.1 mg/m^3 (milligram per cubic meter), chromate-
21 containing etching solutions are not practical for use. Thus,
22 "drop-in replacements" for chromium-containing compounds are
23 needed for etching solutions that otherwise would contain
24 chromium.

1 Sodium metatitanate, potassium titanate and titanium dioxide
2 have been found to be well-suited as "drop-in replacements" for
3 chromium-containing compounds in conventional metal surface
4 etching solutions which typically include, in addition to sodium
5 dichromate, potassium dichromate or chromium trioxide, various
6 other less toxic or non-toxic components. The PEL of the
7 titanium compounds is 15 mg/m³, and thus, the solutions provide
8 highly effective, non-toxic, metal alternatives to solutions
9 which otherwise would include chromium-containing compounds.

11 DESCRIPTION OF THE PREFERRED EMBODIMENT

12 The present invention will hereafter be described in detail
13 with reference to the following embodiments.

14 The preferred embodiments of the present invention are non-
15 chromate metal surface etching solutions for aluminum, aluminum
16 alloys, steel and titanium which include a titanate or titanium
17 dioxide in place of a chromium-containing compound in a metal
18 surface etching solution that otherwise would include chromium.
19 For example, it is known that a solution containing 1 liter of
20 distilled or deionized water, 300 grams of sulfuric acid, 60
21 grams of sodium dichromate dehydrate and 1.5 grams of seed
22 aluminum provides an excellent aluminum and aluminum alloy
23 etching solution. However, as explained above, such chromate
24 containing solutions pose serious health risks.

1 It has now been found that sodium dichromate dihydrate
2 present in the foregoing conventional aluminum and aluminum alloy
3 etching solution can be replaced with sodium metatitanate or
4 potassium titanate without having to alter the various other non-
5 chromate constituents therein or the method of employing the
6 solution. Thus, an etching solution for aluminum and aluminum
7 alloys that otherwise would contain sodium dichromate dihydrate,
8 a highly toxic compound, can be rendered non-toxic.

9 In such cases, the aluminum or aluminum alloy to be etched
10 is first bathed in an etching solution comprising distilled or
11 deionized water in an amount ranging about 0.5 liter (L) to 1.5
12 L, sulfuric acid in an amount ranging from about 150 grams (g) to
13 450 g, sodium metatitanate or potassium titanate in an amount
14 ranging from about 10 g to about 150 g and bare aluminum in an
15 amount ranging from about 0 g to about 5 g. The aluminum or
16 aluminum alloy is immersed in the bath from about 5 minutes to
17 about 20 minutes while the etching solution is maintained at a
18 temperature of about 120° F to about 180° F. Immediately after
19 removing the aluminum or aluminum alloy from the bath, it is
20 rinsed by spraying it with tap water for about 5 minutes. This
21 is contrary to prior art methods for applying chromium-free
22 solution wherein the solution typically is not rinsed from the
23 metal but rather is allowed to dry thereon forming a polymer
24 layer. Thereafter, the aluminum or aluminum alloy is soaked in
25 deionized water and then dried at a temperature of about 120° F

1 to about 140° F. Bonding layers to the metal substrate is
2 performed within about 16 hours of drying.

3 Similarly, it has been found that titanium dioxide can
4 replace chromium trioxide in a metal surface etching solution for
5 stainless steel and titanium which otherwise typically includes 1
6 part by weight (pbw) chromium trioxide and 4 pbw deionized water.
7 More particularly, etching stainless steel typically requires two
8 baths which include two different solutions. For example, a
9 pretreatment bath or first bath for stainless steel which
10 includes a solution of 2.5 pbw sodium metasilicate, 1.1 pbw
11 tetrasodium pyrophosphate, 1.1 pbw sodium hydroxide, 0.3 pbw
12 nacconol and 95 pbw deionized water is required to clean the
13 stainless steel. A second bath is further required which
14 includes an etching solution containing 1 pbw of chromium
15 trioxide and 4 pbw of deionized water. The present invention
16 provides a "drop-in replacement" for chromium trioxide in the
17 foregoing steel and titanium etching solution.

18 Therefore, according to the present invention, stainless
19 steel to be etched is first immersed in a pretreatment bath
20 including sodium metasilicate in an amount ranging from about 1
21 pbw to 5 pbw, tetrasodium pyrophosphate in an amount ranging from
22 about 1 pbw to 4 pbw, sodium hydroxide in an amount ranging from
23 about 0.5 pbw to 2.0 pbw, nacconol in an amount ranging from
24 about 0.1 pbw to 1.0 pbw and deionized water in an amount ranging
25 from about 90 pbw to 95 pbw. The steel is immersed in the

1 pretreatment solution for about 5 minutes to 15 minutes while the
2 solution is maintained at a temperature of about 120° F to about
3 180° F. Thereafter, the steel is rinsed thoroughly in water
4 before being immersed in a second bath or etching bath which
5 includes titanium dioxide in an amount ranging from about 0.5 pbw
6 to about 6 pbw and deionized water in an amount ranging from
7 about 2 pbw to about 10 pbw. The steel is immersed in the
8 etching bath from about 10 minutes while the etching solution is
9 maintained at a temperature of about 140° F to about 190° F. The
10 stainless steel is then washed in cold running deionized water
11 and dried in a forced-draft oven at less than 140° F. Thus, like
12 the etching solution for aluminum and aluminum alloys described
13 above, the etching solution of the present invention for steel is
14 not dried thereon thereby forming a polymer layer on the surface
15 of the steel. Bonding to the stainless steel's surface is best
16 performed as soon as the metal's surface cools.

17 Etching titanium also requires that the metal be bathed in
18 two baths that include two different solutions. Typically, a
19 first bath containing 400 ml (milliliter) of 38% hydrochloric
20 acid, 40 ml of 85% phosphoric acid and 20 ml of 52% hydrofluoric
21 acid is required to clean and etch the surface to the titanium.
22 Thereafter, a second bath is employed which contains an etching
23 solution comprising 1 pbw chromium trioxide and 4 pbw deionized
24 water.

1 Therefore, according to the present invention, titanium to
2 be etched is first immersed in a first bath including a solution
3 comprising about 350 ml to about 450 ml of a 38% solution of
4 hydrochloric acid, about 35 ml to about 45 ml of a 85% solution
5 of phosphoric acid and about 10 ml to about 30 ml of a 52%
6 solution of hydrofluoric acid. Thereafter, it is immersed in a
7 second bath or an etching bath, like the bath for stainless
8 steel, which includes titanium dioxide in an amount ranging from
9 about 0.5 pbw to about 6 pbw and deionized water in an amount
10 ranging from about 2 pbw to about 10 pbw.

11 More particularly, titanium to be etched employing the
12 foregoing solutions is first cleaned with a cloth wetted with
13 trichloroethane in order to degrease the surface. It is
14 preferred that wiping occurs in one direction only. This serves
15 to remove dirt. Thereafter, the titanium is immersed in the
16 first bath or pretreatment bath for about 5 minutes to about 15
17 minutes at a temperature of about 120° F to about 180° F. The
18 titanium is then rinsed thoroughly in water before being immersed
19 in the second bath or etching bath from about 5 minutes to about
20 20 minutes at a temperature of about 120° F to about 180° F.
21 Thereafter, the titanium is washed in cold running deionized
22 water before being dried in a forced-draft oven at $225 \pm 25^{\circ}$ F
23 for 1 hour. Again, the etching solution is not dried on the
24 surface of the metal. The bonding surfaces of the titanium are
25 primed within about 4 hours of etching.

1 While the preferred embodiment of the non-chromate metal
2 treatment solution and method of applying same has been described
3 in detail above, various modifications and variations of the
4 invention are possible in light of the above teaching. As an
5 example, the composition of the surface treatment mixtures and
6 the duration of treatments of various surfaces can be varied
7 without deviating from the scope of the invention. It is
8 therefore understood that within the scope of the appended claims
9 the invention may be practiced otherwise and above described.